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Final Report on Grant
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Study of Supercritical Dense Fluids"

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- 1, ~~ix~~ Validity of the rough hard sphere model of liquids to describe transport and relaxation behavior of simple dense fluids;
- 2, ~~ii~~ Angular relaxation in fluids can be approximated as occurring through a sequence of uncorrelated binary collisions;
- 3, ~~iii~~ Importance of many-body correlation effects on self-diffusion which depends on transfer of linear momentum.
- ✓ iv) Analysis of relaxation and transport data yields the hard core diameters and their temperature dependence.
- 4, v) The results provided experimental verification of the molecular dynamics calculations for hard sphere systems, and
- ✓ vi) The hard sphere model fails both at high densities and low densities ($\rho < 2\rho_c$).
- ✓ vii) The hydrodynamic Stokes-Einstein equation in the slipping boundary condition is found valid.
- 5, ~~viii~~ Applicability of the rough hard sphere model of liquids to describe relaxation and transport processes in binary mixtures.

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1. Dynamic structure of supercritical dense fluids

1.1 Hard sphere model of fluids

Recent evidence indicates that many physical properties of liquids may be determined to a large extent by the size and shape of the atoms or molecules composing them. In particular the molecular dynamics studies by Alder and collaborators (1970) have elucidated many aspects of the static and dynamic behavior of hard sphere fluids and contain many of the basic physical ideas later developed by other authors. This picture of fluids is based on the idea that when the liquid density is high (approximately twice the critical density), the molecules are so closely packed that the forces between particles arise almost exclusively from the harsh short ranged repulsive forces between nearest neighbors. Using this idea the static structures of several liquids have been successfully calculated by depicting them as hard sphere systems and neglecting the slowly varying attractive forces.

Based on a successful prediction of the static properties of liquids, it is important to find the extent to which their dynamic properties can be explained in terms of hard sphere systems. A major problem in this type of analysis, however, is to determine which hard sphere system (i.e., what hard sphere diameter) to associate with a particular liquid.

There were several main goals of our systematic studies of supercritical dense fluids:

- i) First, to find the best effective hard sphere diameter and its temperature dependence for various fluids such as SF_6 , C_4F_8 , CFCI_3 , CF_4 by using the density dependence of the NMR spin-rotation relaxation rates.
- ii) Second, to establish the relationship between the angular momentum correlation times and the Enskog relaxation time.
- iii) Third, to compare the experimental self-diffusion coefficients for the fluids studied with those predicted from the hard sphere theory.
- iv) Four, to show whether the ratio of the linear momentum correlation time to the Enskog relaxation time follows the predictions of molecular dynamic calculations.
- v) Five, to establish the high density and low density limits of the applicability of the hard sphere theory.
- vi) Six, to determine whether dynamic properties of binary mixtures can be described in terms of the hard sphere model.
- vii) Seven, to test the applicability of the hydrodynamic Stokes-Einstein equation at a molecular level.

1.2 Angular momentum relaxation and self-diffusion in SF₆, CFC1₃ and C₄F₈

The NMR ¹⁹F spin-lattice relaxation times, T₁, and self-diffusion constants D have been measured in dense fluids of SF₆, CFC1₃, C₄F₈ as a function of temperature and pressure over the density and temperature ranges given in the specific papers listed in Section 6. Densities and viscosities (C₄F₈) have also been determined. The relaxation mechanism for the fluorine nuclei is dominated by the spin-rotation interactions and therefore the analysis of the T₁ data yields the angular momentum correlation time, τ_J. On the other hand, the NMR spin-echo technique directly measures the self-diffusion coefficient, D, and thus provides information about the linear momentum correlation time, τ_p.

In the theory of liquids and dense supercritical fluids two quantities which are of fundamental importance are the rotational diffusion coefficient D_R and the translational or self-diffusion coefficient D. For this reason a great deal of experimental and theoretical work has been devoted to understanding the relationship of these diffusion coefficients both to other properties of the fluid and to each other. D_R and D may both be determined from the NMR measurements and are related to correlation times by the following expressions

$$D_R = (kT/I)\tau_J \quad , \quad (1)$$

$$D = (kT/m)\tau_p \quad . \quad (2)$$

In Eq. (1), I is the moment of inertia and τ_J is the angular momentum correlation time. In Eq. (2) m is the molecular mass and τ_p is the linear momentum correlation time.

The angular momentum correlation time is defined as an integral over a normalized time correlation function,

$$\tau_J = \int_0^\infty \frac{\langle J(0) \cdot J(t) \rangle dt}{\langle J^2 \rangle} \quad (3)$$

where J is the molecular angular momentum and the brackets indicate an average over the equilibrium ensemble. Since the correlation times τ_J and τ_p reflect the time that is required for a molecule to lose memory of its initial respective momenta, they may be expected to be closely related to the molecular collision frequency. The analysis of the correlation times, which is presented, is based on the assumption that at high densities a fluid may be approximated by a system of hard spheres whose collision frequency is given by the Enskog theory.

If the events which modulate the magnetic field at the fluorine nuclei may be approximated as an uncorrelated sequence of binary collisions Chandler (1974) has shown that

$$\tau_J^{-1} = b(T) \tau_E^{-1}, \quad (4)$$

where τ_E^{-1} is the Enskog collision frequency for hard spheres and $b(T)$ is a constant reflecting the efficiency with which angular momentum is transferred at a collision. This quantity, $b(T)$, may be slightly temperature dependent but should be independent of density. The Enskog collision frequency was calculated using the Carnahan-Starling approximation for the equation of state of hard spheres.

The self-diffusion coefficient D of a real fluid can be approximated by the self-diffusion coefficient of a rough hard sphere fluid D_{RHS}

$$D \approx D_{RHS} = A D_{SHS} = A(kT/m)\tau_E, \quad (5)$$

where D_{SHS} is the diffusion constant for a smooth hard sphere fluid and A is a parameter less than 1, the magnitude of which reflects the effect of the coupling between the translational and rotational motions in the liquid. If A equals one then the liquid behaves as a perfectly smooth hard fluid with no coupling. In order to calculate the theoretical D_{RHS} we used the expression for D_{SHS} obtained by Dymond (1974) by fitting the computer molecular dynamics results by Alder et al. (1970)

$$D_{SHS} = 0.1901(kT/m)^{1/2} \sigma(\sqrt{2}/n\sigma^2 - 1.384) \quad (6)$$

Analysis of the experimental T_1 data enabled us to obtain, σ , the hard sphere diameter of the individual fluids and temperature dependence of σ 's. The results of the analysis are given in Table I.

Table I

Hard Sphere Diameters for fluids Studied^a

Molecule	σ_0 (Å)	T_0 (°K)	$d\sigma/dT$ (Å°K ⁻¹)
CFC1 ₃	5.03	341	1×10^{-3}
SF ₆	4.81	296	$\sim 1 \times 10^{-3}$
C ₄ F ₈	5.65	232	0.9×10^{-3}
CF ₄	4.15	298	0.8×10^{-3}

$$^a \sigma_T = \sigma_0 - d\sigma/dT(T-T_0)$$

The hard sphere diameter are found to be decreasing with increasing temperature as a result of the finite slope of the repulsive potential for a real fluid.

The agreement between the experimental T_1 data and the theoretical T_1 values calculated on the basis of the rough hard sphere theory was excellent for densities higher than twice the critical density. The hard sphere diameter as given in Table I were used in the calculations. The important conclusion of this set of experiments is that angular relaxation in fluids composed of molecules close to a spherical shape can be described in terms of the hard sphere model, i.e., τ_J follows the Enskog τ_E times and no effects due to many-body correlations were found at densities $\rho > 2\rho_c$. The hard sphere diameters which were obtained from the analysis of the T_1 spin-rotation relaxation data were used in expressions given in Eqs. (5) and (6) to calculate the theoretical self-diffusion coefficients.

We just showed that angular relaxation in SF_6 can be approximated as occurring through a sequence of uncorrelated binary collisions. If this is also the case for linear momentum, then one would expect that the ratio of D/D_E to be independent of the packing fraction. As expected, this ratio is strongly density dependent reflecting the effect of many body correlations. For all fluids studied we obtained excellent agreement between the experimental D values and those calculated on the basis of the rough hard sphere theory. Both at high densities $\rho\sigma^3 > 0.93$ and densities lower than $2\rho_c$ we found deviations from the predictions of the rough hard sphere model of liquids.

In the case of self-diffusion at lower densities, deviations from the hard sphere result due to attractive forces were found. Thus, in addition to increasing the collision frequency in fluids at intermediate and low densities, the attractive forces seem to have the additional effect of enhancing the cooperative phenomena (microscopic vortexing) which have been shown to influence the translational motion of hard spheres. In a general sense our studies provided ample evidence for the following statement: Any serious experimental attempt to characterize the molecular dynamics in a fluid must include the separation of the effects of the density and temperature on the molecular motions, namely, one has to carry out measurements at high pressures.

1.3 CF_4 relaxation at $\rho < 2\rho_c$

In order to determine the low density limit of the applicability of the hard sphere model we decided to study fluorine spin-lattice relaxation times

in carbon tetrafluoride in the temperature range $1.20 \leq T/T_c \leq 1.64$ and the density range $0.28 \leq \rho/\rho_c \leq 2.98$. This covers the fluid region from the dilute gas up to dense fluid. The reason for choosing CF_4 was the fact that this molecule is a spherical top with well characterized molecular constants and is very stable thermally.

Following the analysis outlined in Section 1.1, we calculate a ratio τ_E/τ_J ($=b$) over the complete density range. A plot of b vs. ρ in Fig. 1 for different isotherms showed an interesting departure from the rough hard sphere theory. Above twice the critical density b was constant within experimental error. However, at lower densities, we found a definite increase in the value of b . This breakdown of the RHS model at lower densities may be attributed to the increasing importance of attractive forces. At high densities the attractive forces are negligible because of the screening effect by the short-range repulsive forces. As the density is lowered the screening of the attractive forces becomes less effective. Another indication that this breakdown in the rough hard sphere theory is caused by attractive forces is the variation of b with temperature at constant density. With increasing temperature, attractive forces will become less important and the deviations from the theory would be smaller at higher temperatures. That the value of b at low densities deviates less from the high density value with increasing temperature substantiates our conclusion that it is the attractive forces between the molecules causing the deviations from the theory.

1.4 Validity of the hydrodynamic Stokes-Einstein equation at the molecular level

The availability of the viscosity and diffusion data over a wide range of temperatures and pressures makes it possible to test the validity of the well-known Stokes-Einstein equation at the molecular level. This relationship between viscosity and self-diffusion coefficient is given by

$$D = kT/C\pi\eta a \quad , \quad (7)$$

where a is the radius of the molecule and C is a numerical factor which is equal to 6 for the sticking boundary condition and 4 for the slipping boundary condition. We have shown that this expression is approximately valid and that the factor C varies between 3.5 to 5.5 for different molecules. The pressure and temperature dependence of the self-diffusion and viscosity vary over a large range but C remains essentially constant equal to 4.

Alder et al. (1970) have tested this relationship in their molecular dynamics calculation for hard sphere fluid and found that the Stokes-Einstein relationship is remarkably well obeyed over a wide range of densities and the value calculated corresponds to that obtained for the slipping boundary condition. One may conclude that the Stokes-Einstein relationship is well obeyed for the molecular fluids studied.

1.5 Binary mixtures of CF_4 and inert gases

Related to the phenomenon of self-diffusion is the mutual diffusion in binary mixtures. An extension of the RHS model to binary mixtures has been shown to fit mutual diffusion coefficients in several mixtures. Once again, the analysis yields a roughness parameter, "A", and two molecular diameters. Another property which has been interpreted by the RHS model and of more direct relevance to this specific study is the angular momentum correlation time, τ_J .

There are, however, some important questions which still must be answered in order to determine the extent of applicability of the RHS model to angular momentum transfer: (1) Can an extension of the RHS model for angular momentum relaxation to binary mixtures successfully describe the experimental results as was demonstrated for mutual diffusion? (2) How sensitive are the deviations from the RHS model at low densities ($< 2\rho_c$) to the magnitude of the inter-molecular attractive forces? (3) How strongly does the "roughness" parameter, b, depend on molecular shape and are there other factors besides shape which determine its magnitude?

In an attempt to answer these questions we have performed NMR experiments on mixtures of CF_4 with argon and with neon. The ^{19}F nuclear spin-lattice relaxation time, T_1 , has been measured in CF_4 -Ar and CF_4 -Ne mixtures over a pressure range of 100 to 2000 atm and a temperature range of 0 to 100°C at 0.6, 0.25 and 0.10 mole fraction of CF_4 .

The model we used to interpret our results was an extension of the RHS model to binary mixtures. In binary mixtures we can have collisions between CF_4 molecules, and CF_4 -inert gas collisions which will be effective in angular momentum relaxation. The total relaxation rate will be the sum of two terms-- the collision frequency of one CF_4 molecule with other CF_4 molecules, and the collision frequency of a CF_4 molecule with inert gas molecules. Each of these terms is multiplied by a corresponding rotation-translation coupling parameter.

Perhaps the most important result of these calculations is the magnitude of the coupling parameters b_{12} 's. When comparing the values of $b_{\text{CF}_4-\text{X}}$ with those of $\text{CF}_4 - \text{CF}_4$ collisions we see that

$$b_{\text{CF}_4 - \text{CF}_4} \gtrsim b_{\text{CF}_4 - \text{Ar}} > b_{\text{CF}_4 - \text{Ne}} .$$

This progression makes sense physically since it is in order of relative sizes and masses. What the differences between $b_{\text{CF}_4 - \text{Ar}}$ and $b_{\text{CF}_4 - \text{Ne}}$ indicates is that for collisions between unlike molecules there are other factors in addition to the shape or "roughness" of the interacting molecules. The parameter b may be a complex function of size, mass and attractive forces in addition to molecular shape. For argon, as the density decreases, b increases. A similar trend though more pronounced was noticed for pure CF_4 . This trend was taken to indicate that the collisional efficiency for the transfer of angular momentum increases because of the larger role of attractive forces at lower densities. The deviations from the RHS model at lower densities can be arranged by order of magnitude as:

$$\text{CF}_4 - \text{CF}_4 > \text{CF}_4 - \text{Ar} > \text{CF}_4 - \text{Ne} .$$

This is exactly the order one would predict on the basis of the magnitude of the attractive forces between the different pairs of molecules. This constitutes further evidence that it is attractive forces that are important in the deviations from the RHS model.

1.6 Conclusions

The systematic experimental studies discussed briefly above enabled us to arrive at the following main conclusions of general character:

- i) Validity of the rough hard sphere model of liquids to describe transport and relaxation behavior of simple dense fluids.
- ii) Angular relaxation in fluids can be approximated as occurring through a sequence of uncorrelated binary collisions.
- iii) Importance of many-body correlation effects on self-diffusion which depends on transfer of linear momentum.
- iv) Analysis of relaxation and transport data yields the hard core diameters and their temperature dependence.
- v) Our results provided experimental verification of the molecular dynamics calculations for hard sphere systems.

- vi) The hard sphere model fails both at high densities and low densities ($\rho < 2\rho_c$).
- vii) The hydrodynamic Stokes-Einstein equation in the slipping boundary condition is found valid.
- viii) Applicability of the rough hard sphere model of liquids to describe relaxation and transport processes in binary mixtures.

2. Mechanism of reorientation in several molecular liquids

2.1 Fluorobenzene-d₅

The reorientational correlation time τ_θ and the angular momentum correlation time τ_J are fundamental quantities characterizing the molecular rotational motions in a liquid. The correlation times as obtained for example by NMR are the zero frequency Fourier transforms of the normalized correlation functions. For example, the measurements of the NMR quadrupolar spin-lattice relaxation times yield $\tau_{\theta,2}$ depending on the second-order Legendre polynomial.

It is quite understandable that there has recently been considerable interest in theoretical and experimental studies of τ_J and τ_θ and their relationship in liquids. For small angular step reorientation in the rotational diffusion limit ($\tau_J \ll \tau_\theta$) Hubbard has derived the relationship between τ_J and τ_θ . Gordon removed the restriction of small angular steps and proposed a generalized extended diffusion model for linear molecules which allows angular steps of arbitrarily large size. Extended diffusion processes designed as J diffusion and M diffusion were proposed. So far the determination of τ_θ and τ_J in dense liquid region has generally been limited to temperature dependence studies. If one used both pressure and temperature as experimental variables in an NMR experiment, one can separate the effect of temperature and density on τ_θ and τ_J . The pressure dependence of the deuterium and fluorine NMR spin-lattice relaxation times has been measured in fluorobenzene-d₅ in the temperature range from 30° to 350°C. In agreement with our earlier work the extended J-diffusion model described well the reorientation of the fluorobenzene-d₅ molecule even for large values of τ_J .

2.2 Benzylcyanide

Nuclear magnetic resonance relaxation rates have been successfully used to study the anisotropic reorientation of molecules in the liquid state. It

has also been shown that applying pressure to a liquid can have a large effect on the rate of overall molecular reorientation. As part of our broader investigations of the dynamic structure of molecular liquids we became interested in the problem of pressure effects on the internal motions of groups within a molecule in the liquid state.

In this work the deuterium spin-lattice relaxation times of the two selectively deuterated benzyl cyanides, benzyl-4-d₁ cyanide (I) and α,α -dideuterio-benzyl cyanide (II), were measured as a function of pressure. The relaxation time of I gives a measure of the overall reorientation of the molecule, while the relaxation time of II reflects both the overall molecular reorientation and the internal rotation of the CD₂CN group. Using reported deuteron quadrupole coupling constants, the experimental spin-lattice relaxation times, T₁, were analyzed in terms of the rotational diffusion constants for overall molecular, D_M, and internal, D_I, rotation. The activation volumes for D_M and D_I were calculated. The results reflected the difference in frictional torques connected with the overall and internal rotation and also indicated the presence of inertial effects influencing the internal rotation at higher temperatures.

3. Shear viscosity of liquid monosubstituted benzenes.

The shear viscosity of a fluid is of interest both from a practical engineering viewpoint and also as a fundamental quantity reflecting molecular motions in fluids. In order to better understand this transport property, the density dependences of the shear viscosities of several monosubstituted benzenes were examined. This series of molecules were chosen in an attempt to compare the effect of shape (*i.e.* substituent group size) with the predictions from hard sphere theory. Since the hard sphere model is only strictly applicable to an assembly of hard spheres, one might expect that as a molecule becomes more asymmetric, the model may fail in its predictions.

These data were first analyzed in terms of the rough hard sphere model of liquids. This theory has been described in Section 1.1, for diffusion. Basically this model approximates the measured shear viscosity by η_{RHS} which is equal to a constant *c* times the viscosity (η_{SHS}) for a smooth hard sphere fluid. Two general conclusions can be deduced about the rough hard sphere model of viscosity from these analyses on monosubstituted benzenes. The first

is that in all cases, at high densities ($\rho\sigma^3 > 0.95$), the model predicts a much higher value for viscosity than is experimentally observed. This may be attributed to the fact that the hard sphere fluid is metastable at this density. The second conclusion concerns the constant c , which reflects the amount of rotational-translational coupling in the fluid. In order to successfully predict the density dependences, this constant must be varied. This behavior of c may be related to the non-spherical nature of these molecules. The trend seems to indicate that as the molecule becomes more asymmetric, c changes more with temperature.

4. Laser Raman scattering studies

Use of both NMR and Raman methods provides independent means for obtaining τ_J and $\tau_{\theta,2}$. The tetrahedral spherical top molecule CF_4 affords an excellent system to study, since one can determine τ_J by the F^{19} nuclear spin-lattice relaxation and $\tau_{\theta,2}$ by analysis of Raman band shapes. As discussed in Sections 1.3 and 1.5 the τ_J in CF_4 and its binary mixtures with inert gases have been determined by NMR.

The availability of both τ_J and τ_{θ} correlation times enables us to determine whether the reorientational motions can be described in terms of the J-diffusion or M diffusion models and how does reorientational changes with density and temperature. The theoretical analysis of the experimental data enables us to test available theoretical models for reorientational motions in liquids. Theoretical work on this specific project is still in progress.

5. Instrumentation

In the last several years we gained considerable expertise in high pressure NMR techniques, and as far as the current instrumentation is concerned, there is no other laboratory in the USA and/or abroad with comparable performance features of the NMR experimental system. For the experimental work described in the preceeding sections we had to design and build several new equipment items. Most of the details can be found in the Ph.D. thesis listed in Section 7. At this point we only enumerate the main equipment items developed for work sponsored by the AFOSR grant:

- i) High pressure NMR probe of fluids system for large volume changes;
- ii) Densitometer for large volume changes of fluids;
- iii) Gas compression system;
- iv) Oxygen scavenger system for gases;
- v) Gaseous sample handling system for NMR.

6. List of Publications

Acknowledging for AFOSR Support:

- "Molecular Motions of Fluorobenzene- d_5 in the Dense Fluid Region", J. DeZwaan, R. J. Finney, and J. Jonas, J. Chem. Phys. 60, 3223 (1974).
- "Effect of Pressure on the Overall and Internal Rotation in Liquid Benzyl Cyanide", J. DeZwaan and J. Jonas, J. Phys. Chem. 77, 1768 (1973).
- "Nuclear Magnetic Resonance Relaxation Studies of Reorientation Motions in Liquids at High Pressure", J. Jonas, J. DeZwaan and J. M. Campbell, proceedings of the conference "Molecular Motions in Liquids", Societe de Chimie Physique, Orsay, France, 1973 pp. 359-370, D. Reidel Publ. Co., Dordrecht, Holland 1974.
- "Experimental Evidence for the Rough Hard Sphere Model of Liquids by High Pressure NMR", J. DeZwaan and J. Jonas, J. Chem. Phys. 62, 4036 (1975).
- "Nuclear Magnetic Resonance at High Pressures", J. Jonas, Ann. Rev. Phys. Chem. 26, 167 (1975).
- "Density and Temperature Effects on Motional Dynamics of SF_6 in the Supercritical Dense Fluid Region", J. DeZwaan and J. Jonas, J. Chem. Phys. 63, 4606 (1975).
- "Density and Temperature Dependence of Self-Diffusion and Shear Viscosity of Perfluorocyclobutane in the Dense Fluid Region", R. J. Finney, M. Fury, and J. Jonas, J. Chem. Phys. 66, 760 (1977).
- "Shear Viscosity of Monosubstituted Benzenes in the Dense Liquid Region", R. J. Finney and J. Jonas, manuscript in preparation.
- "Density and Temperature Effects on Angular Momentum Correlation Times of CF_4 in the Supercritical Dense Fluid Region", M. Wolfe, R. J. Finney, and J. Jonas, manuscript in preparation.
- "Effect of Neon and Argon on CF_4 Relaxation in the Supercritical Dense Fluid Region", M. Wolfe, E. Arndt, and J. Jonas, manuscript in preparation.
- "Raman Study of Rotational Motion of CF_4 and CF_4 -Inert Gas Mixtures in the Supercritical Dense Fluid Region", H. Schiemann, M. Wolfe, and J. Jonas, manuscript in preparation.

7. Ph.D. Thesis

Dr. Jack DeZwaan

"Determination of the Effects of Density and Temperature on Molecular Motions in Dense Fluids Using High Pressure NMR", University of Illinois, Urbana, Ill. 1974.

Dr. Ray J. Finney

"High Pressure NMR Studies of Transport Properties in Dense Fluids", University of Illinois, Urbana, Ill. 1976.

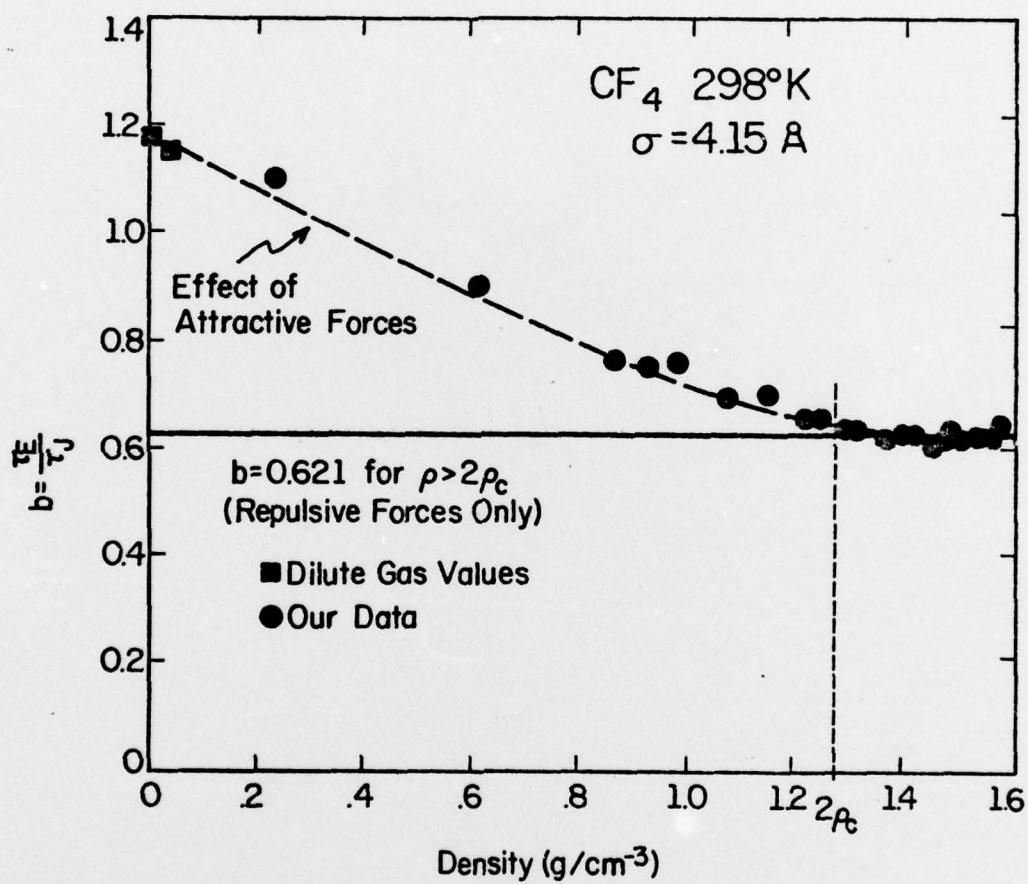


Fig. 1 Density dependence of coupling parameter b upon density in CF₄ at 298°K.